ENERGY INNOVATIONS SMALL GRANT (EISG) PROGRAM

EISG FINAL REPORT

DEVELOPMENT AND CHARACTERIZATION OF IMPROVED SOLID STATE DYE-SENSITIZED NANOCRYSTALLINE SOLAR CELLS

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Abstract

The purpose of this project was to determine methods to reduce the risk involved in the commercial development the dye sensitized nanocrystalline solar cell. The existing state of the art of this new thin film photovoltaic technology holds promise for the reduction of costs of PV, but it suffers from reliability problems due to the use of volatile liquids used to transport charges from the dye. Our investigation involved replacing the liquids with Polythiophenes such as Poly(3-undecyl-2,2'-bithiophene).

Objectives included selecting and testing of a suitable polymer, measurement of the dye and polymer spectroscopically to determine relative energetics, deposition of TiO_2 films via a Sol Gel technique, measurement of the charge carrier dynamics of the dye, polymer, and TiO_2 , and fabrication and testing and optimization of solar cells fabricated with the above materials.

We have selected a hole - conducting polythiophene polymer that is also "dye", and developed techniques to characterize materials suitable for the dye - based solar cells. The devices fabricated with our materials have junction properties that are unique as well as efficient, given that only one layer of TiO_2 and dye was used (surface roughness = 1X). Current voltage characteristics of devices fabricated using our technique are in agreement with the energetics of the components. We have obtained $V_{OC} = 0.8$ V and $J_{SC} = 100$ uA/cm^2 under AM1.5 simulated solar illumination.

We conclude that polythiophene polymers may be utilized in the dye sensitized cell if they function efficiently as dyes in porous or multilayer materials, or if they do not interfere with the standard dye's absorption of light.

Executive Summary

Introduction

A research group at the Swiss Federal Institute of Technology in Lausanne, Switzerland has developed a potentially low cost solar cell based on "sensitizing" organic dyes and materials used in white paint (called *Titanium Dioxide,* TiO_2). It has been confirmed experimentally that the Swiss technology has an overall sunlight to electrical energy conversion efficiency of 7 -10 % under direct and diffuse sunlight. While this conversion efficiency is lower than the 15 % of standard solar cell technology, or photovoltaics, it offers advantages including environmentally friendly components, low temperature processing, and potentially lower costs to consumers. Calculations indicate that solar cells of at least 10 % efficiency could be realized at less than $3/Watt cost. This may be competitive with conventional electricity generation, and the approach could open up new markets in flexible solar cells used for consumer applications such as computers and cell phones, and also in utility - scale power generation. These markets are already over 100 Megawatts per year at approximately six dollars per Megawatt sold. Although patents for the new technology have been issued, there is significant opportunity for assigning intellectual property of further developments that allow it to reach these markets.

The purpose of this project was to determine methods to reduce the risk involved in the commercial development of a new thin film solar cell technology. The existing state of the art of the new technology holds the promise to reduce costs for solar generated electricity, but it suffers from reliability problems due to the use of volatile liquids used to transport charges. Our investigation involved replacing the liquids with suitable solids. It is the term "suitable" that we elucidated with various analytical techniques. We chose conductive polymers as the replacement for the liquid, and, specifically, Polythiophenes. Based on the goal of developing a solar technology, this project supports the Renewable Energy Technologies PIER subject area.

Objectives

- Task 1 Select and test a suitable dye and polymer
- Task 2 Measure the dye and polymer spectroscopically
          to determine relative energetics
- Task 3 Conduct synthesis of TiO_2 films
- Task 4 Measure the charge carrier dynamics of the dye, polymer, and TiO_2
- Task 5 Fabricate solar cells using above materials
- Task 6 Test solar cells, and improve dye, polymer, and TiO_2 properties
-

Implicit in the last task was the development of methodologies and techniques for linking the measurement of the component materials to the final device. A primary and overall objective was the construction of an energy band diagram useful in the understanding of how the device functions, and to optimize the device output. We wished to determine if charge transfer can occur via the polythiophene, and whether this material absorbs light itself. If so, we wished to know if it interferes and competes with light absorption by the dyes used in the state of the art device, and whether it can replace these dyes.

Outcomes

Our significant conclusions arise from the fact that we have accomplished our tasks. We have:

- Selected a dye that is also a hole conducting polythiophene polymer,
- Constructed energy band diagrams, and developed techniques to characterize materials suitable for the dye based solar cell,
- Fabricated solar cells using sol gel - deposited TiO_2 and the above polymer, and
- Tested solar cell devices, and found that the junction properties are unique as well as efficient (given the geometry we selected).

We have utilized our easy to manufacture TiO_2 , materials, together with spin coated polymers to fabricate solid state solar cells. These devices produced exceptional results given the fact that only a thin layer of polymer and a single layer of TiO_2 was utilized. Current voltage characteristics of devices fabricated using our technique are in agreement with the energetics of the components, and are quite encouraging when compared to existing technology based on sensitization mentioned above. We obtain as much as can be expected from a single layer of sensitizer (polymer), and a flat TiO_2 surface given the energy band diagram, and spectroscopic characterization. With our techniques, we have obtained voltages over 0.8 V and current densities of 100 micro-amps per square centimeter of active area outside in sunlight, or inside under simulated solar illumination.

It should be noted that in almost every case there is an improvement in cell performance. This is attributed to an annealing process that is taking place between the polymer layer and the TiO_2 yielding better electrical contact and enhancing charge transfer processes.

Our project's primary objective was to fabricate, optimize, and understand the function of low - cost solid state photovoltaic (solar) cells based on polymer sensitized TiO_2 materials. Based on our results, commercial feasibility is possible if the emphasis is

now placed on utilizing porous or multil-ayer materials. The most critical issue for future work will be the extension of our results to higher surface area materials that can result in higher photocurrents.

We recommend polymers that either:

- function efficiently as dyes in porous or multilayer materials, or
- they do not interfere with another dye's absorption of light, while preserving the favorable properties that we have demonstrated in this study.

Benefits to California

At this point in the research, only potential benefits to California can be qualitatively estimated. Our experimental results support our approach which was advanced using measurements from this study. Taken together, our results allow for the further optimization and study of dye sensitized solar cells. The long term benefits of diversifying our energy portfolio include stabilization of CO_2 levels in the atmosphere, decreased pollution and environmental degradation, and economic benefits to both the United States and to California due to use of resources available within California.

Introduction and Background

The purpose of this project was to determine methods to reduce the risk involved in the commercial development of a new thin film solar cell technology. This technology holds the promise to reduce costs for solar generated electricity, but it suffers from reliability problems due to the use of volatile liquids used to transport charges. Our investigation involved replacing the liquids with suitable solids. It is the term "suitable" that we elucidated with various analytical techniques. Based on the use of solar technology, this project supports the Renewable Energy Technologies PIER subject area.

A research group at the Swiss Federal Institute of Technology in Lausanne, Switzerland (EPFL) has used the blueprint of photosynthesis to produce a potentially low cost solar cell. So simple is this technology that it can be done in a kitchen or a high school lab. An educational kit teaching principles in chemistry and physics with the technology is the first product to make use of the findings of the EPFL[4]. It has been confirmed experimentally that the technology has an overall sunlight to electrical energy conversion efficiency of 7 -10 % under direct and diffuse sunlight [1,2]. While this conversion efficiency is lower than the 15 % of standard technology (see Appendix IV), it offers advantages including environmentally friendly low temperature processing, and potentially lower costs to consumers. Calculations which consider the spectrum of the light utilized by the light absorber, and the materials and processes involved indicate that solar cells of at least 10 % efficiency could be realized at less than $3/Watt cost (see Appendix V). This may be competitive with conventional electricity generation, and the approach could open up new markets in flexible solar cells (on plastic) used for consumer applications (e.g. computers and cell phones), and in utility - scale power generation.
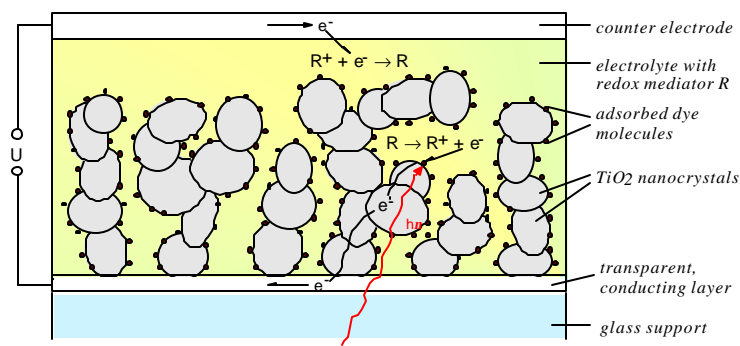
Figure 1. Dye sensitized solar cell schematic showing light absorption, electricity production and mediator (R/R$^+$) regeneration. The objective of the present study involves the replacement of the existing mediators (iodide/triiodide) with materials that could allow for a reliable and practical device (see Appendix for a more description).

There is an increasing interest in combining organic molecules with inorganic semiconductors to create optoelectronic devices. In recent years, combinations of polymer semiconductors (e.g. polythiophenes and poly(p-phenylene) vinylene's) with colloidal nanocrystals of wide bandgap inorganic semiconductors (e.g., TiO_2 or CdS)

have been investigated, as well the blending of these types of materials [3-9]. These polymers are being aggressively researched in terms of low cost and high area light emitting diodes (LEDs) and in solar cell technology. The most promising solar technology has been reported by Grätzel and co-workers in their development of a ruthenium dye-sensitized nanocrystalline TiO_2 solar cell with a solar conversion efficiency of approximately 10% and quantum efficiencies of over 90% [1-3]. The current limitation of this nanocrystalline solar cell technology is the use of low viscosity nitrile-based liquid solvents that are used to carry the redox mediator. These electrolytes allow for an efficient solar cell energy converter, but are difficult to seal and maintain.   Our goal was to utilize materials being developed for other fields of electronics to solve the stability problem by replacing the electrolyte with conductive polymers. If the identified objectives can be met, then the use of this hybrid device will present significant price breakthroughs in solar cell and light detector technology, since the processing of the materials is simpler than conventional p-n junction solar cells technologies mentioned above, as well as the current state of the art for dye sensitized solar cells.

The dye-electrolyte combination can be replaced by a dye-polymer combination, or by a single conjugated polymer layer bringing together the functions of light absorption and charge (i.e. hole) transport [3,8]. Our objective in this phase of the research was to explore the latter configuration and to develop specific techniques for materials selection that would lead to efficient and reliable dye sensitized cells. Prior work identified a number of materials that were already yielding encouraging results when compared to liquid junctions. The liquid junction can be effectively replaced with stable semiconducting thiophene-containing polymers [8,9]. Our goal was to investigate the possibilities for creating photovoltaic cells based on these conjugated polymers and TiO_2 , and to develop methods for rationally screening materials that can be used to produce practical, efficient, and economic, devices.

Project objectives were to:

- Task 1 Select and test a suitable dye and polymer.
- Task 2 Measure the dye and polymer spectroscopically
             to determine relative energetics.
- Task 3 Conduct synthesis of TiO_2 films.
- Task 4 Measure the charge carrier dynamics of the dye, polymer, and TiO_2 .
- Task 5 Fabricate solar cells using above materials.
- Task 6 Test solar cells, and improve dye, polymer, and TiO_2 properties.

Implicit in the last task was the development of methodologies and techniques for linking the measurement of the component materials to the final device. A primary and overall objective was the construction of an energy band diagram useful in the understanding of how the device functions, and to optimize the device output. These objectives were met by using the methods described in the *Project Approach* section that follows. We expanded the text of the original *Statement of Work* under *Tasks and*

Milestones to include "dye and polymer" where it originally read merely "dye". This is understood from the description of the tasks, since it is the coupling, and understanding of, both these items that will result in an "Improved Solid State Dye-Sensitized Nanocrystalline Solar Cell"

The basic approach derived from our goal of understanding the energetics of the dye, of the thiophene polymer hole conductor, and the TiO_2. This can lead to an improved solid state dye-sensitized nanocrystalline solar cell. We refined and applied electrochemical and spectroscopic characterization techniques to a number of alkyl - substituted thiophene - based polymers that are potential solid electrolytes for nanocrystalline solar cells based on dye sensitized TiO_2 nanoparticles. Together with the published values in the literature for the TiO_2 and Ru dye [1-3], our goal was to construct an energy band diagram for use in the understanding of the functioning of the devices made with various potential materials.

Comparing Solid State and Liquid Solar Cells
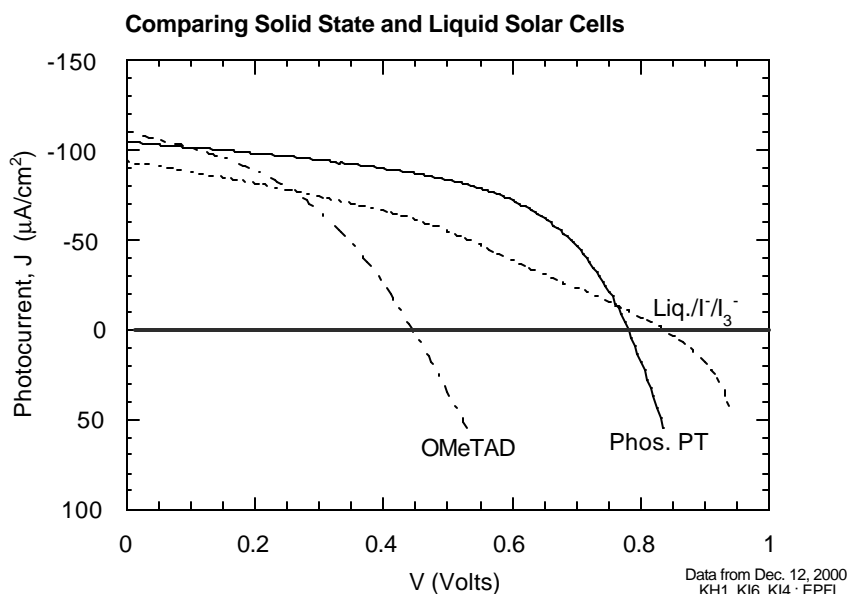
Figure 2. Comparing the J-V curves in the light for three hole conductors in the Ru dye sensitized solar cell. The Liq./I^-/I_3^- represents the standard liquid junction cell, and the OMeTAD represents a solid state hole conductor that has produced the highest conversion efficiencies to date [3].

Through our collaboration with the EPFL in Switzerland, it was found that Polythiophene (PT) polymers have already shown great promise as hole transport layers in solid state dye sensitized solar cells (see Fig. 2). Prior work has made the comparison between alternative hole conductors:

> Phosphonated and Alkyl Polythiophenes [8],
> Liquid (Liq.) electrolyte (a iodide-iodine-triiodide mediator) [1-2], and
> Spiro-OMeTAD [3].

The interaction between the dye and polythiophenes was found to be as good as the other hole conductors. What was significant about these tests is that all other conditions were similar, and the photovoltaic devices were fabricated utilizing a single

thin (100 nm), flat, non-porous TiO_2 film, and a single layer of Ru dye together with the above mentioned hole conductors. This is a simplified system when compared to the usual multiple - layer porous nanocrystalline TiO_2 layers used in the liquid - based dye sensitized solar cell. In this approach, which we adopted for this study, the light passes only once though the system, first through the TiO_2 and dye, and then the polymer or hole conductor. Our study configuration is not one that would be used in a practical PV application, but it provided us with very useful insights. It may also have spin off applications that include detectors of light that may be useful in medicine, control of energy efficiency, or in spectroscopy (e.g. materials characterization). The configuration was chosen to isolate and focus on one of the three fundamental questions that should be answered for a hole conductor in the dye sensitized solar cell configuration:

- Does charge transfer (i.e. hole) via the solid hole conductor?
- Does this hole conductor absorb light itself? If so, does it interfere and compete with light absorption by the Ru dye, or does it efficiently inject?
- Can one place this hole conductor into all the pores of nanocrystalline TiO_2?

Our chosen experimental configuration was selected to address only the first and second items. The selection of the experimental configuration was made because prior attempts to utilize organic and inorganic hole conductors in the nanocrystalline dye sensitized solar cell have convoluted all these aspects at once [3-7,9] Results were thus difficult to interpret and optimize.

Using the Stages and Gates terminology, from the technical and engineering viewpoint, the Stage 1 (Idea Generation), and Stage 2 (Technical Analysis) aspects were fundamentally completed at the time that the EISG award was made. Marketing analysis was also reviewed from the well-established PV community (Appendix V & IV). Stage 3 (Research and Bench Scale Testing), as well as proof of feasibility, were the targets of the research conducted under this Energy Innovations Small Grant Program.

Report Organization

In the next section, the project approach will be described, as well as the testing methods and procedures. Project outcomes and results will then be presented as well as discussion interpretation, conclusions, and recommendations for future work. A glossary of terms is provided as well as references cited. Appendices are also provided with details on background material and the procedures and methods utilized.

Project Approach

Next, we will present specific aspects of our experimental approach used to meet our objectives.

- **Task 1. Selection and testing of a suitable dye and polymer**

We selected both the anthocyanin dyes of our earlier studies [1], and the Ru dyes[5] used in the efficient described in the background section [2,3]. We have found that certain substituted polythiophenes can act as both dye and hole transport layers. We have characterized a number of thiophene - based polymers as potential solid electrolytes for nanocrystalline solar cells based on sensitized TiO_2 . The ultimate goal is to improve the efficiency of the solar energy conversion device, by either modifying the structure of the polymers, or synthesizing a better hole transport material. This is possible only if characterization techniques are developed. We have characterized two different types of substituted polythiophene polymers, a phosphonated polythiophene (P3PUT), and an alkyl substituted polythiophene (P3UBT and P4UBT). The P3UBT, was made with the Sugimoto process with $FeCl_3$ oxidant [11]. It was Stereo-irregular, or regio-random. The P3PUT and P4UBT was made with the Negishi-type condensation, and was 90% stereoregular [10]. We have utilized $CHCl_3$ (chloroform) and Tetrahydrofuran as a solvents. The polymer's average molecular weight was 6,000 - 7,000 g/mol. The molecular weight distribution ranged from 1498 (for 4 thiophene rings per molecule) to approximately 6500 (for 17 thiophene rings per molecule).

Important parameters that we focused on included:

> Polymer morphology and the affect of deposition techniques,
> Polymer solubility, doping and stability,
> Polymer energetics and optical properties, and
> Characteristics of the solar cell device utilizing the polymers.

Our primary focus was the creation of a direct analogue of the liquid device and the utilization of "large bandgap" polymers that will not block the light from the dye.

- **Task 2. Measure the dye and polymer spectroscopically**
  to determine relative energetics

This characterization involved various spectroscopic methods, including UV-Vis absorption and fluorescence spectroscopy. These measurements are essential to construct the energy band diagram, and are also useful as an input parameter for the transient absorption spectroscopy measurements using a femtosecond Ti - sapphire laser. These spectroscopic characterizations aid in the understand the fundamental photophysics, and mechanisms of charge transfer in the polymer, and the physical and electronic coupling to the oxide semiconductor (TiO_2).

Spectroscopy was performed on a solution of the polymers (in THF or Chloroform). The UV-visible spectra were measured on a Hewlett-Packard diode array spectrophotometer (with 2 nm resolution. Fluorescence measurements were undertaken on a Perkin-Elmer fluorometer to show observable fluorescence at room temperature and establish the quantum yield of this fluorescence using a standard solution of a known luminescence material (Rhodamine 6G).

We also performed electrochemical measurements to characterize the polymer materials. This electrochemical analysis was performed on thin films of the polymers deposited on conductive glass, and we have combined this information with the spectroscopy to construct an energy band diagram. The electrochemical measurements on the Polythiophenes were taken using a Solartron SI 1280B instrument purchased using funds from the EISG grant.   A $Ag^+/AgCl$ reference electrode was employed in the standard three electrode arrangement, with 0.1 M Tetrabutylammonium tetrafluoroborate (TBATFB), in reagent grade acetonitrile, serving as a supporting electrolyte. Scan rate was 20 mV/sec. A (porous glass) frit tube was used to introduce the reference electrode so that the KCl within it would not contaminate the acetonitrile electrolyte.

Cyclic voltammagrams (C-V) of the polymers were recorded to determine the redox potential and the approximate position of the HOMO energy levels. UV-Visible spectroscopy was used to determine the band gap of the materials and hence the LUMO energy levels of the polymer.   Quantum yields of the polymers were determined via fluorescence since this is an important parameter to establish radiative and non-radiative recombination rates. From these separate measurements, energy band diagrams were constructed relative to TiO_2 to illustrate and elucidate the mechanisms of how the polymer(s) function in the device (from a thermodynamic perspective).

- **Task 3. Conduct synthesis of TiO_2 films**

We have synthesized TiO_2 thin films for use in the solar cell devices via a sol gel technique, and have characterized these materials via SEM and electrochemical analysis. These films were found to be morphologically and electrochemically equivalent to the Spray pyrolysis deposited materials used in earlier studies [8]. It was desirable to have TiO_2 films that would block the passage of the hole conductor to the SnO_2:F glass substrate. These passivating films of TiO_2 were called "blocking". Our studies utilized "flat" (dense) TiO_2 in order to establish the effectiveness of hole transfer while not having the complexities of the polymer light absorption and TiO_2 pore filling to compound the measurements. If the research continues, our approach will also utilize porous and nanocrystalline TiO_2 materials, to allow for the production of larger photocurrents and power outputs.

A sol-gel based synthesis for TiO_2 flat thin films was developed as an alternative to the spray pyrolysis method. The sol gel procedure was based on that found in the literature with some modifications [12]. The porosity and roughness of the titania thin films were characterized via cyclic voltammetry and electron microscopy (SEM) techniques. Cyclic

voltammetric (C-V) experiments were preformed to determine if the films blocked the passage of a redox active electrolyte. This was determined from the suppression of the oxidation and reduction peaks of the electro-active species (further details are in Appendix I). These C-V's were compared to that of spray pyrolysis films. Scanning Electron (SEM) and Atomic Force microscopy (AFM) were used to determine thickness and surface roughness of the films.

- **Task 4. Measure the charge carrier dynamics of the dye, polymer, and TiO$_2$**

Femtosecond laser spectroscopic data was obtained to determine excited state lifetime (kinetics). Transient absorption experiments (dynamics) were performed using a femtosecond Ti-sapphire laser system, involving a pump-probe scheme [13]. Electrons and holes were produced using a pump wavelength of 390 nm, with probing at a wavelength of 790 nm or 850 nm. The transient absorption of the polymer samples have been measured. The sample optical density at the pump wavelength was adjusted to 1.0 and recorded. We have measured both polythiophene with the femosecond laser system, and have overcome our initial instability problems associated with the measurements by using suitable measurement conditions (See Appendix III).

- **Task 5 & 6. Solar Cell Fabrication and Characterization**

We have utilized the sol gel TiO$_2$ and spin coated polythiophene polymers to fabricate a solid state solar cell (see Appendix II). The device configuration is also shown in the Appendix. We have focussed our attention on the building of reproducible solid state solar cells. These cells are based on sol gel "flat" TiO$_2$ films that are spin coated on conductive glass, and are then used as a substrate for a spin coated layer of an alkyl - substituted polythiophene polymer. Finally, a die cast layer of the polymer is applied, and a carbon powder contact is applied. The input aperture and graphite powder mask are 0.25 cm^2 in area. Light enters through the TiO$_2$ side, and passes once through the device. The positive contact is a graphite powder with a Cu or Al foil strip pressed on top of the carbon using a glass slide and clamps. Negative contact is made to the TiO$_2$ side of the device via the SnO$_2$:F glass. The fabricated device is characterized in the dark, and under illumination via current voltage (J-V) and impedance analysis. These devices produced comparable results to the devices previously fabricated with similar materials at the EPFL in Switzerland [8].

In most cases, the cells were then sealed via a non-porous epoxy. Cells were tested for resistance via a multimeter. If cells produced a resistance of less than 0.15 - 0.2 Mohm, they were normally discarded. Current-voltage (IV) curves were then obtained under AM 1.5 equivalent intensity using our Solartron SI 1280B electrochemical measurement unit and halogen lamp. Measurements were also taken outside as a comparison and to check the lamp calibration. Impedance spectroscopy was also obtained utilizing the SI Solartron 1280B to determine interface properties between the TiO$_2$ and polymer.

Project Outcomes

- **Task 1 & 2. A Suitable polymer was selected as dye and mediator, and band diagrams were created from spectroscopic data**

The two types of the polymers utilized in this study are shown in Fig. 3. P3UBT became the focus of the analysis. A spectroscopic study of a chloroform solution of P3UBT solution was undertaken. The emission (fluorescence) spectrum was obtained by exciting at the absorption maximum. The quantum yield of the emission was found to between approximately 10% (see Figure 4). The P3PUT had a yield of ca 1%.
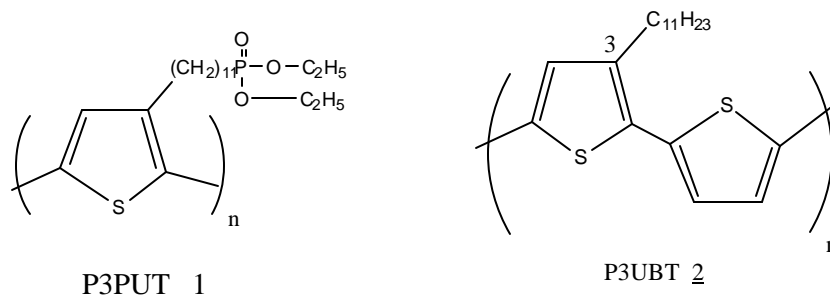
Figure 3. Chemical structures of the Polythiophenes (PT) studied, P3PUT & P3UBT.

Quantum Yield study of P3UBT in CHCl$_3$
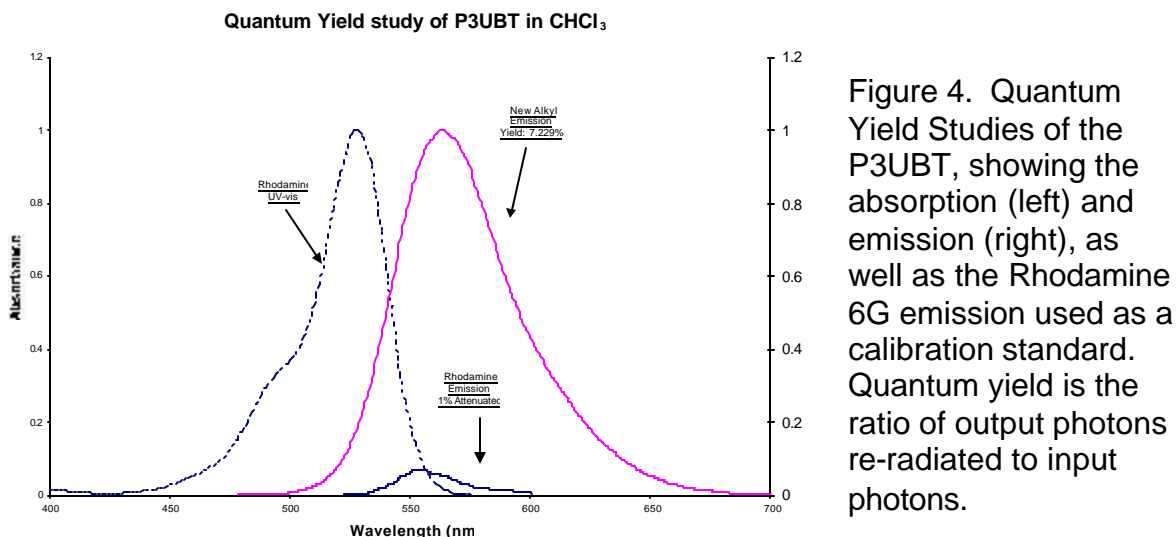
Figure 4. Quantum Yield Studies of the P3UBT, showing the absorption (left) and emission (right), as well as the Rhodamine 6G emission used as a calibration standard. Quantum yield is the ratio of output photons re-radiated to input photons.

High luminescence is but one of the desirable properties of an ideal PV material. During our electrochemical measurements (see Fig. 5), we observed a strong electrochromic change. Upon oxidation (+ bias), the films turn to a neutral gray color. The film's reflectivity changes as well as the film morphology. This may indicate macroscopic structural changes like the roughness of the films. The changes were reversible through three cycles. The broad features of the C-V curve, may be because the oxidation is a multi-step process, or be a result of a different (micro) environments for some of the PT molecules in the film.

P3UBT-F CV Plot

J(mA/cm²)

E (V vs. Ag/AgCl)

Figure 5. Electrochemistry (C-V) of the P3UBT. The oxidation peak is indicated as 1.1 V and the reduction peak is 0.9 V vs the reference electrode. From this we can estimate the ground state energy level.

From the electrochemistry of films Phosponated PT, or P3PUT, and P3UBT deposited on conductive glass, a portion of the energy band diagram c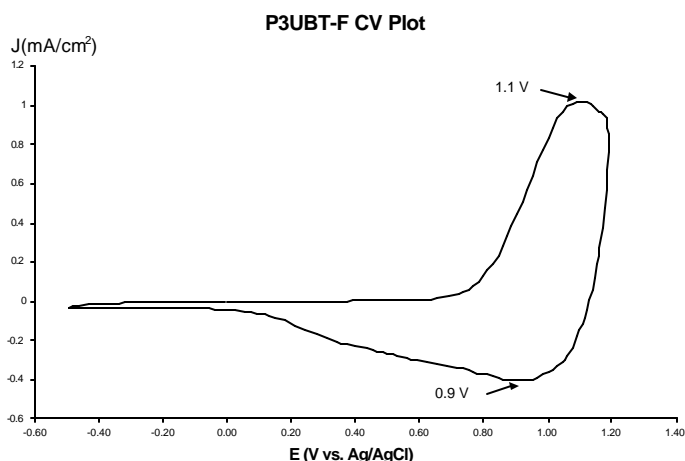an be constructed and the ground state redox potential of +1.0 to 1.1 V vs. NHE can be assigned. Although this will not significantly affect the devices made without Ru dye, this value is marginal, since a larger value will put the ground state (HOMO) below the Ru dye's ground state (see Fig. 7). This would make regeneration of this dye difficult, and may result in poor fill factors and photocurrents for Ru dye sensitized cells using polythiophenes as hole conductors and mediators. The LUMO or higher level of the dye can be estimated from the optical density of the films deposited on quartz substrates. The optical density was plotted in accordance with the idea that the polymers posses a "direct type" bandgap (difference between higher and lower conduction levels) [11]. As with other solar cell materials like GaAs and CdTe, a plot of the square of the product of absorption coefficient and input photon energy yields the bandgap energy at the x-intercept. A direct bandgap is desirable for solar cells since it typically means light is absorbed strongly, and so less of the material is required (lowering materials costs).

P3UBT-F Film Bandgap and Absorbnace Plot
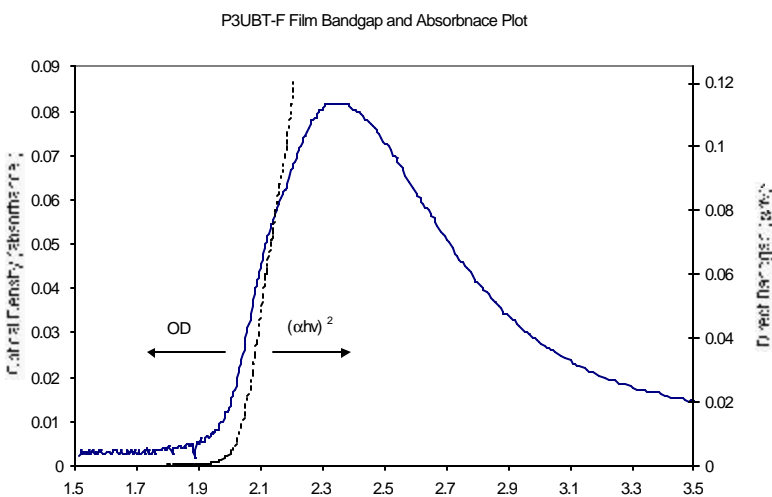
Figure 6. Bandgap plot of P3UBT. The curve at the right is the Optical Density, OD, or Absorbance of the film of P3UBT. At the left is an extraplation based on a direct bandgap. From this we can estimate energy difference between HOMO and LUMO [11].

Spectroscopic measurements on Polythiophene films yielded bandgaps in the range 1.9 to 2 eV (Fig. 6). With this information and the information from the previous two figures, the absolute positions of the higher and lower energy levels of the polythiophenes could be estimated and referenced to the vacuum level as well as to the Normal Hydrogen Electrode (NHE). From this and the published values in the literature a band diagram could be constructed (see Fig. 7) that can allow insights into the functioning and optimization of devices which use the polythiophenes and TiO_2 together with Ru dyes, by themselves.

Figure 7. Energy band diagram of the polythiophenes together with the other components of the dye sensitized solar cell. This was constructed with the values from the previous two figures. Also indicated is the expected voltage, V, from the device.

- **Task 3. Synthesis of the TiO$_2$ films yielded blocking contacts**

TiO$_2$ Thin Film Porosity Electrochemical Characterizatio

J(mA/cm^2)

Blank (No TiO$_2$ Film)

Anodic

TiO$_2$ Film

Cathodic

E (Volts)

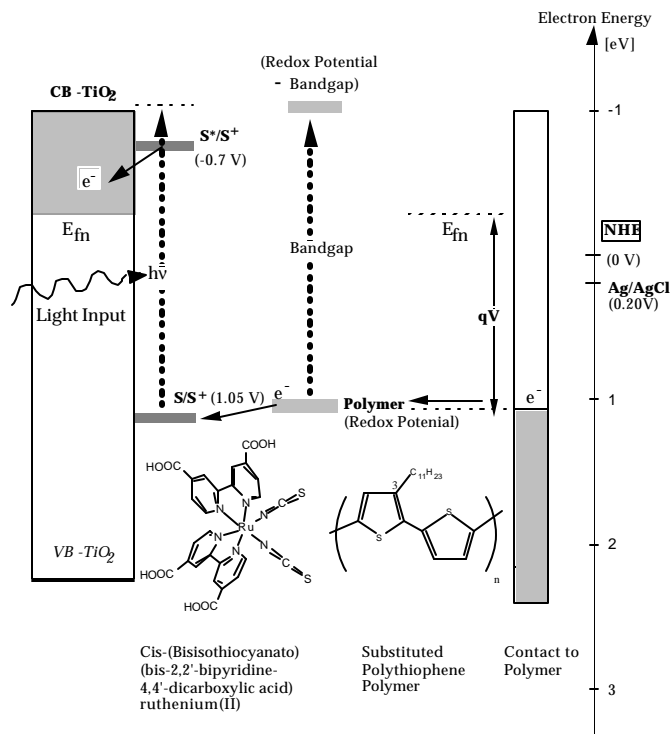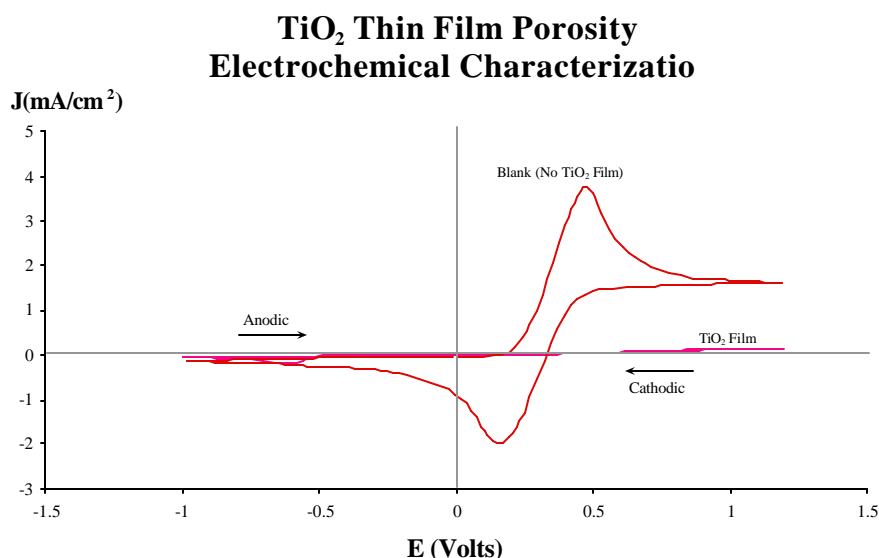Figure 8. Blocking characterisitics of the TiO$_2$ film produced via the sol gel technique. The electrolyte was a 0.1 M Fe(CN)$_6$ $^{3-/4-}$ solution in deionized water. This technique was developed to as a performance control measure on the TiO$_2$ gel films.

The sol gel (TiO$_2$) films were immersed in a 0.1 M Fe(CN)$_6$ $^{3-/4-}$ solution and compared to the behavior of a blank consisting of bare glass. If the electrode blocked the passage of the electrolyte, a suppression of the oxidation and reduction peaks was observed. We optimized our TiO2 synthesis and deposition technique (Appendix I) and succeeded in making uniform and good quality films suitable for our studies. SEM and AFM images were also used to verify the findings obtained from the above electrochemical analysis.

- **Task 4. Laser Dynamics indicated a suitable excited state lifetime**

Femtosecond dynamics studies were conducted on of the alkyl – substituted polythiophene P3UBT that was used to fabricate most of the solid state dye sensitized solar cells that were constructed. A typical transient absorption plot for one time scale is shown in Figure 9.   A decay constant of 200 - 250 ps is obtained from a simple exponential fit to the data. The time scale in Fig. 9 indicated is pico-seconds (ps). This measurement of the polymer was made in THF. The probe wavelength was 790 nm, and the resulting transient absorption (Δ A, or delta A) of the polymer is indicated. From our prior work on dyes, and the work of others, these results indicate an excited state lifetime which is sufficient for charge carrier injection [1] and efficient PV devices based on dye sensitization. We were unable to perform measurements of this type on PT polymer – TiO$_2$ composite systems due to complications arising from our inability to extract a pure composite system for study, and the conflicting signals that both materials would generate.

P3UBT-F Transient Absorption Long Time Scale
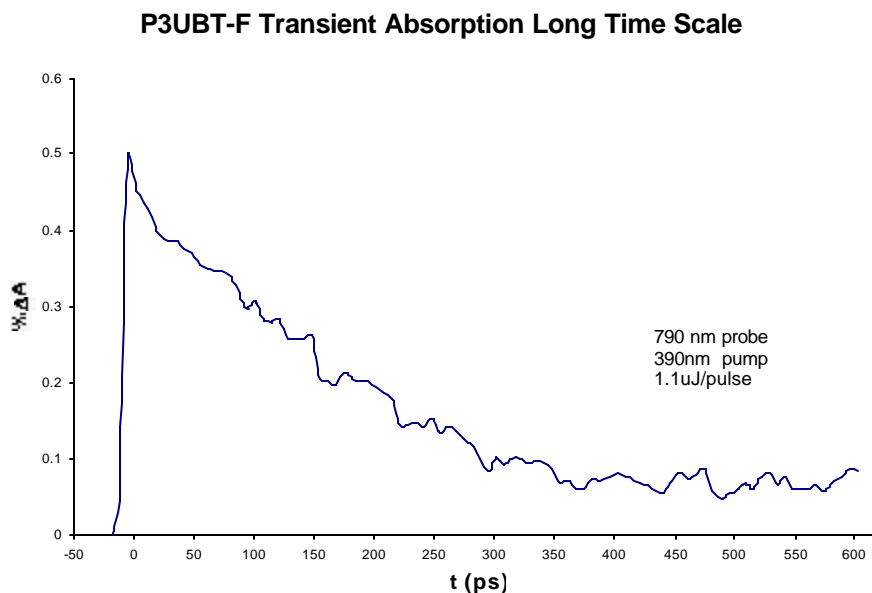
Figure 9. Transient Absorption (laser dynamics) for the P3UBT hole conductor.

Ultrafast laser studies at 4 different powers (10, 3.5, 1.1, and 0.5 J/pulse) on the P3UBT-F polymer/THF solution did not yield any power dependant features. A plot of optical absorption before and after the laser measurements indicated that the polymer showed between 1 and 5 % degradation. This is due to the fact that the solution was not purged of oxygen, and so there is some degradation of the polymer. No serious degradation at 390 nm (pump wavelength) or at 790 (probe wavelength) is apparent.

- **Tasks 5 & 6. Solar Cells were fabricated tested and improved**
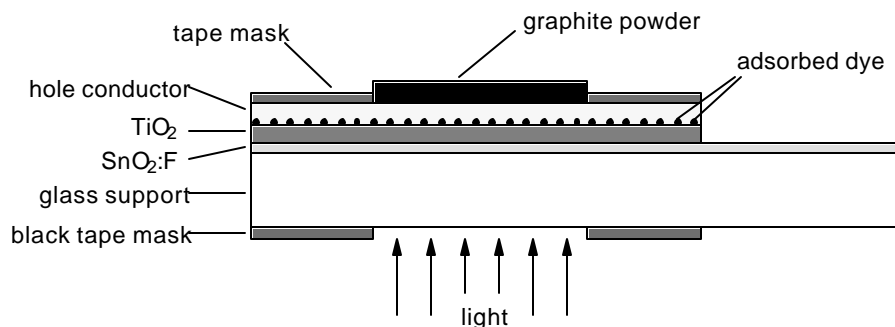
Figure 10. Solar Cell configuration used to fabricate solar cells with the TiO_2 and Polythiophenes.

We have utilized the sol gel TiO_2 and spin - coated layers of polythiophene -based polymers to fabricate and test over 100 solid state solar cells. Our device configuration is given in Figure 10. We have overcome our initial difficulties regarding the reproducibility and low electrical output of our devices. This was accomplished via the introduction of a heating step prior to the spin coating of the polymer, and also via the use of a die cast layer of polymer deposited on the film via the use of a Kapton tape mold. We have found that these are critical steps in obtaining reproducible, high-performance TiO_2/PT solar cells:

1) One must anneal the TiO_2 films at 450 °C (30 min. in air) prior to spin coating the PT polymer or applying the dye.   One can store annealed TiO_2 films in anhydrous Ethanol to protect the film from the air.

2) We have found that better results can be obtained by a drop cast/die cast method (See Appendix II). Instead of letting the polymer drop freely on the TiO_2 film, we mask off a portion of the TiO_2 film with 4 pieces of Kapton (Scotch) tape. This is a yellow-colored tape widely used in semiconductor processing. We leave a central square area of TiO_2 uncovered so that a "mold" or channel can be formed. This channel can hold a small amount of liquid containing the solution containing the polymer. The PT solution is deposited in this channel, and the PT film dries slowly within it.

With this technique, we have obtained V_{OC} = 0.8, J_{SC} = 60 - 70 uA/cm^2 for measurements outside, or at AM1.5 simulated illumination (see Fig. 11). We performed AFM imaging measurements of the surface of the polymer to understand that surface tension effects, and this lead us to the improved deposition technique.
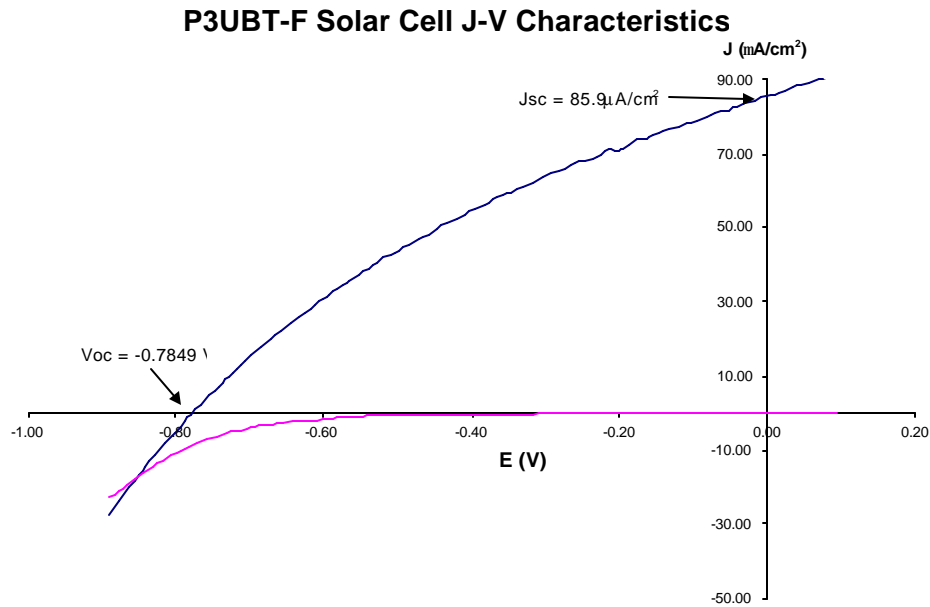
- 17 -

P3UBT-F Solar Cell J-V Characteristics

Figure 11. J-V curve of a completed solar cell using the materials studied in this project. The figure shows the current – voltage (J-V) characteristics for a solid state solar cell in the dark (lower curve), and illuminated (upper curve) with simulated (AM1.5) sunlight. Rectifying behavior was observed, together with a strong photovoltaic effect, as predicted by our energy band diagram (See Appendix IV & glossary for definitions).

We have utilized the sol gel TiO_2 , as well as Spray Pyrolysis TiO_2 materials [8], together with the spin coated polymers to fabricate functioning solid state solar cells. These devices produced exceptional results given the fact that only a thin layer of polymer and a single layer of TiO_2 was utilized. J-V characteristics of devices fabricated using our technique are in agreement with the energetics of the components reported above (band diagram, Fig. 7), and are quite encouraging when compared to existing technology based on sensitization. We obtain as much as can be expected from a single layer of sensitizer (polymer), and a flat TiO_2 surface given the energy band diagram, and spectroscopic characterization previously described. The devices behave as a diode that does not obey the principle of superposition of light and dark characteristics. The maximum solar conversion efficiencies was calculated from the product of the fill factor, voltage, and current as

$$h = \frac{0.4 \ \cdot \ 0.8 \ \text{V} \ \cdot \ 100 \ \times \ 10^{-6} \text{A/cm}^2}{100 \times 10^{-3} \ \text{W/cm}^2} \times 100 = 0.032 \ \%$$

The 100 mW/cm^2 the denominator represents the input solar power at AM1.5 illumination. These studies utilized "flat" (dense) TiO_2 in order to establish the effectiveness of hole transfer while not having the complexities of the polymer light absorption and TiO_2 pore filling to compound the measurements. Future studies can

utilize porous and nanocrystalline TiO_2 materials with the confidence that the first and 2nd questions posed in the *Background* section is understood. The efficiency of our devices is admittedly small, but this was not the focus of our study, rather it was the development of rational selection techniques for the replacement of the liquid - based electrolyte. Porous and multilayer (nanocrystalline) TiO_2 has a surface roughness of over 500 X [1-3]. With only 200 layers like the one reported above, efficiencies are predicted to be over 6 %, well within the range for practical applications, but with a much improved device reliability and with facile manufacturing techniques.

Time Series of P3UBT-F Solar Cell
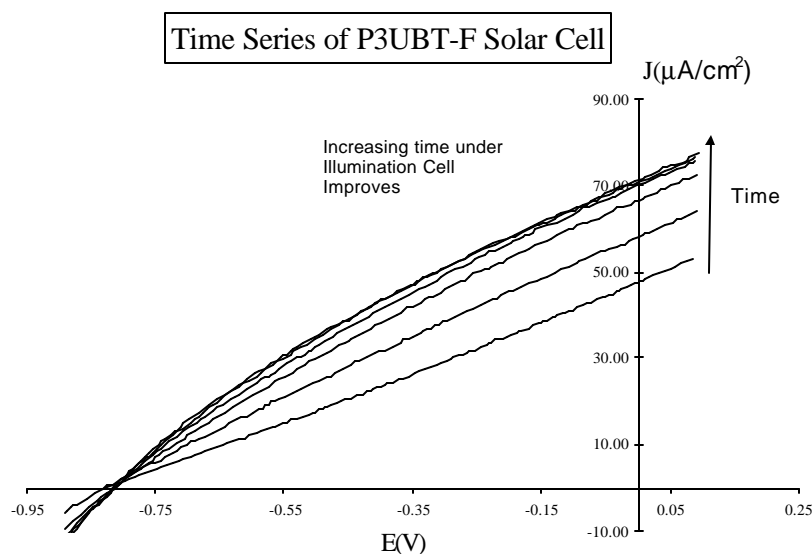
Figure 12. The time evolution under illumination of a P3UBT polymer solar cell.

It should be noted that in almost every case there is an improvement in cell performance (see Fig. 12). This is attributed to an annealing process that is taking place between the polymer layer and the TiO_2 yielding better electrical contact and enhancing charge injection.

To further characterize the device, we utilized impedance analysis using our Solartron impedance analyzer. Figure 13 shows the impedance spectroscopy of the device as characterized in Figure 11. We undertook device modeling using simple equivalent circuit models which include resistance, and capacitance. Our devices behave under illumination like a 1 nano-Farad (nF) capacitor in parallel with a 28 K (kOhm) resistor, and in series with a 3 K resistor. These measurements allowed for useful feedback on the development of fabrication techniques. The same analysis allowed an understanding of the polymer - TiO_2 electrical junction. Figure 12 shows a Mott-Schottky plot for the device after a brief exposure to light. This measurement was made in the dark.   If the cell is measured without prior exposure to light, the corresponding Mott-Schottky plot is flat. A measurement made of a standard silicon (Si) cell yields the

well - known behavior similar to the -1 V to +1 V scan. Typically one extrapolates this curve to the x - intercept to obtain the "built in" voltage (-0.88 V for Si), but this is not possible with our devices. The junction formed between the TiO_2 and the Polythiophene is this atypical, and is most likely established via photoconduction and doping by light. We have thus established one of the mechanisms proposed in our grant proposal.

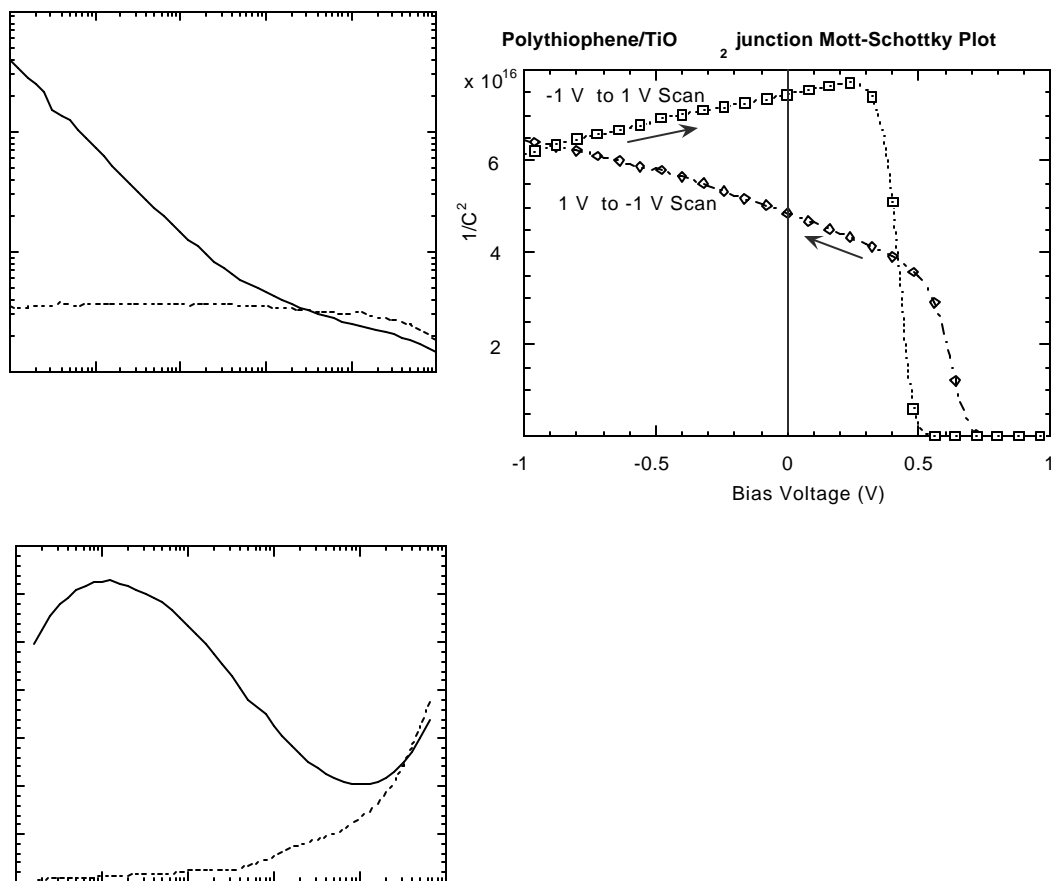Figure 13. Impedance, Z, analysis vs. ac frequency of the same solar cell as in the previous two figures. The plots at the left demonstrate the photoconduction mechanism (photodoping) in the polythiophenes. The plot at the right is a Mott-Schottky measurement of the capacitance, C, of the device as a function of applied bias, V.

Conclusions and Recommendations

Our significant conclusions arise from the fact that we have accomplished our tasks:

- **Selected a dye that is also a hole conducting polythiophene polymer,**
- **Constructed energy band diagrams, and developed techniques to characterize hole conductors suitable for the dye sensitized solar cell,**
- **Fabricated solar cells using TiO_2 and the polymer, and**
- **Tested solar cell devices, and found that the junction properties are unique as well as efficient (given the geometry we selected).**

A significant finding of our collaborators at the EPFL is that the P3UBT does sensitize the TiO_2 in the absence of the dye, while the P3PUT does not sensitize TiO_2. In other words, the P3PUT merely functions like the iodide/triiodide mediator, as we would wish it as a direct replacement of the liquid - based mediator. It does not function as a dye. In the current study, we collected evidence that can aid in the understanding of why this difference was observed. At UCSC, we examined the results of the electrochemistry and photophysics to find that the two polythiophenes do not appear to have significantly different energetics, (HOMO/LUMO), referenced to the TiO_2 and Ru dye. In this case, they both should inject into the TiO_2, yet only the P3UBT significantly does. We also observe that the P3PUT seems to stick to the TiO_2, (coloring it), implying that it orients its Phosphonate end toward the TiO_2 surface. This leads to the idea that the above observations are due to the difference in the kinetics of electron injection between the two polymers, and can be explained by the orientation of the PT polymers on the TiO_2 surface. We conclude that if one wishes only to employ the polymer in the role of a hole conductor, the orientation found in the P3PUT is desirable. The mode of attachment for the P3PUT is probably a "hydrogen bond" type involving the TiO_2 -OH groups. Phosphonated dyes , are found to attach strongly when compared to the normal carboxylic acid linkages. The exact nature of the bonding could later be explored through FTIR spectroscopy.

One might consider the use of the P3UBT as a dye and hole conductor, and exclude the Ru dye, but our findings have suggested that this may be problematic. The configuration this represents is the same as that used in organic solar cells over the years, and the approach suffers from the low mobility of charge carriers in the organic
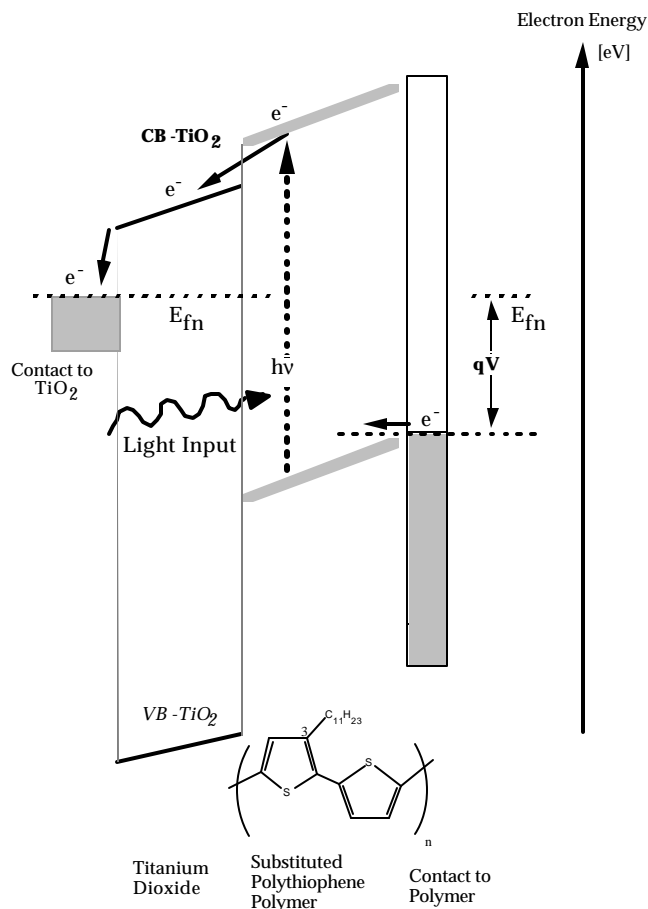
Figure 14. Energy Band diagram of our PV device viewed as a heterojunction solar cell. The polymer at the right functions as the "dye" or light absorber, as well as the hole transport material.
This approach is problematic, but does lead to important conclusions. Although the polythiophenes are promising hole conductors, their use without other dyes is limited unless higher mobilities can be obtained.

layer (e.g. polymer), and thus low solar conversion efficiencies have been observed. The contribution of dye sensitized solar cell is the use of only a thin layer of organic to do the job of light absorption, while allowing charge separation to occur in two other materials (i.e. the TiO_2 and hole conductor). Thicker absorber materials do not improve the performance unless their properties are carefully selected. One can understand this from the basic equations that describe solar cell performance.

There are two types of device efficiencies used to characterize and understand solar cells and detectors. The solar conversion efficiency has already been presented (and in Appendix IV). The 2nd efficiency is the Induced Photo-Current Efficiency, IPCE, sometimes called the quantum efficiency. It is the number of electrons output (at short circuit) per input photon at that wavelength. The IPCE is measured at the short circuit point where the voltage on the [monochromatic] J-V curve is close to zero. In our P3UBT/TiO_2 flat solar cells (without dye) both electrons and holes are generated in the PT and the electrons must diffuse to the polymer-TiO_2 interface to be collected. This is

the "standard" heterojunction geometry used in many thin film solar cells. The short circuit currents, J_{SC} , we measured are dependant on the IPCE. The quantum efficiency, or IPCE, is approximated by the well known equation for this "backwall illumination" case,

$$IPCE \approx \frac{1}{\left(1 + \frac{1}{\alpha L}\right)}$$

3

where L is the diffusion length (e.g. for electrons in the PT), and α is the absorption coefficient of the light absorber (e.g. the PT polymer). It is a measure of the length a charge carrier can diffuse during it's lifetime, and is given by

$$L = (D t)^{1/2}$$

4

where D is the diffusion constant given by the Einstein relation,

$$D = \frac{k\,T(°Kelvin)\,\mu}{q}$$

5

The term k is Boltzman's constant, q is the elemental charge (constant), T is the absolute temperature, and μ is the mobility of the charge carrier. What one concludes from these equations and our results is that unless the mobility of our PT polymers are larger, then D, L, IPCE, and J_{SC} will all be limited. In this case, there is not much hope for this approach unless better (higher μ) materials are found. Note that for our P - type PT materials, the hole mobility measured by other researchers 10^{-4} cm^2/V sec [1] . This gives one an idea of our μ values. We predict that one can not expect much more than we have reported on from our P3UBT solar cell in the present configuration.

Using the polymer as both mediator (hole conductor) and the light absorber (dye") is problematic. We have found that the photocurrent using a thick layer of P3UBT polymer gives approximately the same photocurrents as those with a single layer of Ru dye or polymer. This would imply that only a single layer of organic material is efficient for charge injection into TiO$_2$. This the fundamental conclusion about organic "dyes" and has resulted in the creation of the dye sensitized solar cell configuration in the first place. The above equations demonstrate that unless electron or hole mobilities of over 1 cm^2/V sec are utilized, the photocurrents and thus the efficiencies will be limited.

On the other hand, if we utilize porous TiO$_2$, and a dye, and a more transparent hole conductor, as is done for the liquid - based dye sensitized solar cell, then the device does not rely on the mobility in the light absorber (in this case, the dye). Instead, the mobility, μ, value and the IPCE are described by a different set of parameters and equations than in the previous case. It is likely that is described by the "illuminated frontwall" case with inclusions of surface recombination, S, determined by the

interaction of the electron and hole at the TiO_2/hole conductor interface. This could be influenced by putting something on the surface of the TiO_2 along with the dye (a "co-adsorbate). The relevant mobility value is most likely the mobility of the hole in the composite TiO_2/hole conductor matrix. Although this approach has more hope than the former geometrical configuration, it still suffers from the limitation of low mobility of the hole conductor. The preceding exercise can supply some theoretical background as to why we conclude that the use of transparent PT polymers together with porous or multilayer TiO_2 offers the best chance for increasing the device performance further. The configuration that is suggested is :

Underlayer/Porous TiO_2 / Dye + Transparent version [large bandgap] of our polythiophene polymers. Critical issues to be solved in future work are transparency, and pore filling as mentioned previously in the *Introduction* section.

Our project's primary objective was to fabricate, optimize, and understand the function of low - cost solid state photovoltaic (solar) cells based on polymer sensitized TiO_2 materials. Based on our results, commercial feasibility is possible if the emphasis is now placed on the final fundamental aspect presented in the Introduction section. The most critical issue for future work will be the extension of our results to higher surface area materials that can result in higher photocurrents.
We recommend polymers that either:
- **function efficiently as dyes in porous or multilayer materials, or**
- **they do not interfere with another dye's absorption of light, while preserving the favorable properties that we have demonstrated in this study.**

Both of these approaches may involve modification of the existing materials. Taken together our results demonstrate that the simple interface (TiO_2 - polythiophene polymer) can function efficiently in charge transfer and hole conduction. This result, and our experience in the characterization of the materials, therefore gives us the confidence to proceed with a more complicated device geometry.

A critical factor is charge compensation for the injected electron. In the liquid junction cell, the counter ions can shield and screen the charge as it is transported in the TiO_2 and in the electrolyte. In a solid cell, electrons (- charge) travel one direction, and the holes (+ charge) travel in the opposite direction. Since a space charge layer is unlikely, a compensating charge is required, or the cell will charge up like a capacitor and stop at some limiting current. Work by Bach et al has found that additions of mobile Li+ ions have been shown to help with this problem [3].   One can re-design our PT polymer to help with this mechanism. One can design a kind of "polaron" charge transport mechanism for the hole[1). One can also design in a group on the polymer for Li+ ion transport. Future work should therefore address this interface and junction aspect. Our results, and those of Bach et al, [3], indicate that one possible method for assisting charge injection from the polymer to the TiO_2 would be the adsorption of a dipole molecule onto the surface of the TiO_2. This creates an electric field, which aids in charge separation and inhibits recombination once the electron is in the conduction band of the TiO_2.

Development Stage Assessment

Project Development Stage Activity Matrix

Stages / Activity	1 Idea Generation	2 Technical & Market Analysis	3 Research	4 Technology Develop-ment	5 Product Develop-ment	6 Demon-stration	7 Market Transfor-mation	8 Commer-cialization
Marketing	▓	▓	▓					
Engineering / Technical	▓	▓	▓					
Legal/ Contractual	▓	▓	▓					
Risk Assess/ Quality Plans	▓	▓	▓					
Strategic	▓	▓	▓					
Production. Readiness/	▓	▓	▓					
Public Benefits/ Cost	▓	▓	▓					

- **Marketing**

A marketing analysis has been competed by Dr. Michael Graetzel of the EPFL as well as a business plan. He has enlisted the aid of several companies as license holders to the technology involving the liquid based junction. The configuration described in this report represents improvements to the technology, and so this plan would need to me suitably modified and updated for Stage 4 development. In addition, other markets including low power and low cost consumer power sources need to be considered and an alternative development pathway formulated that would utilize the device's promise as both a detector and a light detector. Industrial partners would need to be identified and accessed.

- **Engineering/Technical**

During this EISG study, we have established 2 of the 3 requirements for a material that can reduce the risk for technology and produce development of a potentially low cost PV solar cell. Further research is needed to extend this result to TiO2 with higher surface areas. Our approach has established several technical and engineering benefits of our materials and selection technique.

- **Legal / Contractual**

U.S. Patents 5,084,365 (Graetzel et al, 1992) and 4,927,721 (Graetzel et al, 1990) have been issued, as well as World Patent WO 91/16719 (Graetzel et al, 1991). Development of additional Intellectual Property is possible through the research described in this report, since it potentially extends the usefulness of the above invention.

- **Risk Assessment/Quality Plans**

A Quality Plan needs to be developed that meets ISO 9004 Quality Management and ISO 9001 Quality Assurance criteria. The Quality Plan will specify quality control criteria including technical performance, safety and environmental performance, in accordance with ASME, AWS, ASTM, IEEE standards, California and federal regulations. Selected elements of the Quality Plan will minimize risks by applying risk reduction techniques with safety analysis methods.

Environmental and Safety issues in the configuration could represent substantial improvements over state of the art PV devices. A full assessment of this aspect has yet to be completed.

A preliminary life cycle analysis of the cost is given in Appendix V. Any updates of this would be made in accordance with Commission requirements and in close collaboration with PIER staff.

- **Production Readiness**

This research is not ready for the production stage. However, as show in the report and in the Appendices, production techniques that meet the goals outlined in the lifecycle analysis and cost estimate have been considered throughout the research. If this research continues, this aspect will be one of the central issues that will be considered. Several PV companies have been contacted, and a literature search competed, and this can serve as a reference as the development process advances.

- **Strategic**

Development of the technology has been linked to PIER policy objectives. This project does not appear to impact other PIER projects at this time, but a full assessment of the projects is necessary, as the findings of this study are relevant to the development of both solar cells and light detectors. These detectors may have applications in other PIER projects. This project is not critically dependent on other projects under development within PIER or elsewhere.

- **Public Benefits / Costs**

At this point in the research, only potential benefits to California can be qualitatively estimated. Our experimental results support our approach which was advanced using measurements from this study. Taken together, our results allow for the further optimization and study of dye sensitized solar cells. We are confident that significant improvements can be made with the fundamental knowledge we have gained during this study. The resulting devices could be cost and performance competitive with existing solar cell materials such as Silicon (Si) and Cadmium Telluride (CdTe). The long term benefits of diversifying our energy portfolio include stabilization of CO_2 levels in the atmosphere, decreased pollution and environmental degradation, and economic benefits to both the United States and to California due to use of resources available within California.

Other benefits already received from this project are the transfer of technology and techniques from the EPFL and from Georgia Institute of Technology. These benefits are more difficult to quantify. There is an educational aspect to our work since it has primarily been carried out by UCSC students. This can have significant benefits both to UCSC, to the University of California system, and to California in general. The methods developed and refined in this study can be applied to the further development of solar cells, as well as light detectors that can be used in a variety of applications including medical, energy, and in the characterization of novel materials for electronics. If this project is successful, and it's findings are fully utilized, a novel low cost solar cell could be produced that could make an impact on energy utilization in California and nationwide.

Endnotes

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4) An educational nanocrystalline solar cell kit is
   available for approximately $40 from:
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5) Ru dyes obtain from:
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Glossary

AFM = Atomic Force Microscope (related to Scanning tunneling Microscope, STM).
AM1.5 = Air Mass 1.5. This is the standard solar spectrum and light output used for
       solar cell measurement. It is related to angle of the sun in the sky.
C-V = Cyclic Voltammetry. An electrochemical characterization technique.
Dye = A chemical pigment molecule or compound that will absorb visible light.
EPFL= Swiss Federal Institute of Technology, Ecole Polytechnique Federal de
       Lausanne
EISG = Energy Innovation Small Grant
HOMO = Highest Occupied Molecular Orbital. The lower energy level of a molecule.
Hole = Site in a crystal where an electron is missing. It is thus positively charged, and
sometimes mobile.
Injection = The transfer of an electron or hole into a semiconductor or solid (a process
in dye sensitization).
J-V = Current density - Voltage (also sometimes called I-V if just current - V is used)
LUMO = Lowest Unoccupied Molecular Orbital. The higher energy level of a molecule.
Mega = The prefix of a unit meaning 1,000,000, or 10^6 of that unit (e.g. Mohm). A
Megawatt is a million watts or a thousand kilowatts.
Mediator = In an photoelectrochemical cell, the mediator is the substance that
maintains (and protects) the neutral electric charge on another substance by becoming
oxidized or reduced. In the dye sensitized solar cell, it is the catalyst present in the
electrolyte between the TiO_2 coated glass and counter electrode.
Micro = A prefix meaning 10^{-6} of a unit (e.g. uA).
Milli = A prefix meaning 10^{-3} of a unit (e.g. mA).
Mohm = Mega Ohm (10^6 Ohms). A measure of electrical resistance.
Nano = A prefix meaning 10^{-9} of a unit.
PV = **Photovoltaic cell** = A device that converts radiant energy (photons or light) into
electricity *(= a Solar Cell).*
PIER = Public Interest Energy Research
P3PUT = Poly[3-(11-diethylphosphorylundecyl)thiophene. A phosponated PT.
P3UBT = Poly(3-undecyl-2,2'-bithiophene). An Alkyl PT
P4UBT = Poly(4-undecyl-2,2'-bithiophene)
PT = Polythiophene. A polymer of thiophene
Ru Dye = cis- SCN $_2$Bis(2, 2' bipyridyl - 4,4' - dicarboxylate) ruthenium(II)
Charge-Transfer Sensitizer.
SEM = Scanning Electron Microscope or Microscopy.
TBATFB = Tetrabutylammonium tetrafluoroborate. Used as a supporting electrolyte.
TiO$_2$ = Titanium dioxide, titania. An inert mineral used in pigments and industry.
UV = Ultra Violet (light in the range from 200 - 400 nm)
Vis = Visible light in the range from 400 - 700 nm.
Voltage, V A measure of difference in electrical potential between two electrodes or
points (in volts).

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Appendix I TiO$_2$ Preparation Procedure

This procedure is modified from the literature [A1].

Substrates for TiO$_2$ film deposition are washed as follows: H$_2$0 (Deionized water, or mili-Q), then isopropanol, a total of three times in succession. This is done on the spin coater at a angular speed of 1000 rpm. Substrates are masked off prior to cleaning with scotch tape. Components of the sol gel mixture are (in the order of mixing):

10 ml 100% EtOH
250 uL milli-Q H$_2$O
Add acid (HNO$_3$ or HCl) to bring pH to about 1-2
750 uL Ti Isopropoxide (TIP)

These components are combined in a beaker while stirring (on a stirring plate) and stirred for a few days prior to using to make a TiO$_2$ film. To avoid undesirable precipitates, the TIP is added last. The TIP is air sensitive, so it is recommended that the TIP be added to the rest of the mixture in the glove box. One checks the pH of the solution after adding the TIP. If it has risen, one adds another drop of acid until it returns to the range specified above. It is recommended to combine the components and to do the TiO$_2$ sol gel synthesis at decreased temperatures (0 °C), but this is not necessary and, from our J-V curves for the TiO$_2$ films in Iron Ferrocyanide electrolyte, we do obtain blocking TiO$_2$ films with sufficient properties for solar cells. Sol gel TiO$_2$ films are made by depositing 100 uL of precursor solution (above) onto the substrate and immediately spinning at an angular speed of 1000 rpm for 60 seconds. They are then fired for 60 min at 100 °C and 450 °C for 30 min. If time is critical, one can decrease the time to 10 min at 450 C and even omit the 1 hour drying time at 100 °C.

A performance measure of these films was determined by cyclic voltammetric (C-V). Experiments were preformed in a three-electrode cell , together with our Solartron SI 1280B electrochemical measurement unit. Bare conductive glass (SnO$_2$:F) as a working electrode, with Ag/AgCl as reference electrode, and Pt wire as a counter electrodes. The three electrodes were immersed in a 0.1 M Fe(CN)$_6$ $^{3-/4-}$ solution. This blank was then run to determined the redox potential of the electro-active species on the bare surface, and then the working electrode was exchanged for one covered with a titania (TiO$_2$) film. If the electrode blocked the passage of the electrolyte a suppression of the oxidation and reduction peaks was observed.

Reference

 [A1] M. Zaharescu, M. Crisan I. Musevic, "Atomic force microscopy study of TiO$_2$ films obtained by the sol-gel method" Journal of Sol-Gel Science and Technology, 1998, Vol. 13 (N1-3), 769-773.

Appendix II

Cell Assembly Procedure

Starting material for the cell fabrication is 1 x 0.5 cm piece of SnO_2:F transparent conductive glass (LOF). This substrate is pre-coated with TiO_2 (via a sol gel technique) and a contact tab of bare SnO_2:F is left on one edge by masking with tape. This is heated in a heat gun at 450 °C for 30 minutes to activate and dehydrate the TiO_2. The glass is removed from the heat gun and cooled on a piece of silica for 60-90 seconds. The slightly cooled glass is placed on the spin coater, a few drops of a 4 mg/ml solution of polymer in $CHCl_3$ is dropped onto the surface and spun at 1000 rpm for 20-30 seconds. The temperature should be such that the $CHCl_3$ should not boil when dropped on the glass. A second spin (2x) is quickly applied with the same solution. For a more homogeneous film, the solution is heated in a hot (~100 °C) water bath before application to the substrate. AFM (Atomic Force Microscopy) work was performed to determine film quality and coverage and thickness, and it was this work that suggested novel methods of applying the polymer materials.

The 2x spun glass is cleaned using cotton swabs and $CHCl_3$. The sides, back and SnO_2 tab must be completely clean of polymer to avoid shorting the cell. Using 3M Kapton tape, the polymer-coated section of the substrate is masked off in order to apply a second layer of polymer; this is called a "die" casting. A 2 mg/ml polymer/$CHCl_3$ solution is used for the die cast to avoid overly thick films. A 0.1 to 0.5 cm^2 section of the polymer coated region is masked with tape and used. Again, the polymer solution is heated to approximately 100 °C before application of the additional layers of polymer. One to two drops are applied to the masked off area, enough to cover the whole surface.

One weakness of this die cast method is its propensity towards inhomogeneous surfaces due to the poor solubility of the polymer and at larger surface areas the surface tension is not great enough to give a consistent film. Therefore, with a given single die cast, only 0.1 - 0.2 cm^2 area can be covered. To overcome this, a technique called "mosaic" die cast was developed. This mosaic casting involves masking off multiple areas one at a time and casting each one individually, creating a mosaic effect. This can be done as many times as necessary to cover a given area. Two methods of assembly have been implemented in this research. The first technique relies on a single "die" cast, while the other uses multiple casts resulting in a "mosaic" application.

Figure AII 1. Solar Cell configuration [A2]
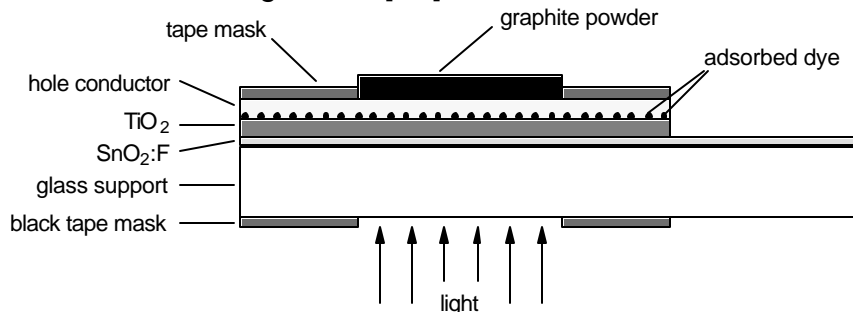
After deposition of the polymer, the tape (mask) is removed and excess polymer is cleaned off the substrate using solvents. After this, black electrical tape (3M) is used to mask the edges around the polymer, leaving the SnO_2 tab uncovered. A small amount of carbon is applied to the surface within the masking, approximately 1-2 mm in height. A cover slide is cut to approximately the same size as the cell and a strip of copper tape is applied to one side. This cover slide is placed so the copper tape is overlapping the carbon electrode, leaving a copper/glass tab opposite the SnO_2 tab. The cell is firmly clamped using binder clips and tested for resistance, current, and voltage. If the cell has a resistance less than 0.15 - 0.2 Mohm, it is considered "shunted" and is discarded. Current - voltage curves can be measured on functioning cells, or the edges of the cell can be sealed using epoxy and left to dry overnight.

Reference

[A2] S. Spiekermann, G. Smestad, J. Kowalik, L. M. Tolbert, and M. Grätzel, "Poly(4-undecyl-2,2'-bithiophene) as a hole conductor in solid state dye sensitized titanium dioxide solar cells", Synth. Met. 2001, 121(1-3), 1603-1604.

Appendix III

Laser Dynamics Procedure

Ultrafast experiments (charge carrier dynamics) were performed with a regeneratively amplified, mode-locked femtosecond Ti-sapphire laser. The laser system and the experimental setup has been described elsewhere [A3]. In brief, pulses of 40 fs in duration with a repetition rate of 100 MHz were generated with 5 nJ/pulse. The laser pulses were subsequently amplified in a Ti-sapphire regenerative amplifier with chirped-pulse modification. Final output pulses were on the order of 150 fs with 350 uJ/pulse energy centered at 780 nm and a 1 KHz repetition rate. The output was then frequency doubled in a KDP crystal to generate approximately 30 μJ/pulse of 390 nm light, which was used to excite the polymer samples, which were contained in a quartz cell of 1 cm optical path. The remaining fundamental (780 nm) is focused into a quartz disc to generate a white light continuum. Experiments were conducted at two wavelengths (790 and 850 nm) and at three different polymer concentrations. The desired probe wavelength was selected by using an interference bandpass filter. The probe beam was split into a sample and reference channel, which were detected by two photodiodes. The signal was processed by a computer-controlled, gated integrator in conjunction with an analog-to-digital converter (ADC). Dividing the sample channel by the reference for each laser shot eliminated pulse-to-pulse fluctuations of the laser beam. The delay between pump and probe beams was controlled via an optical delay line based on a translation stage. Pump and probe beams were focused using a 10 cm focal length lens and cross overlapped over a spot size of approximately 0.5 mm in the sample slightly before the focal point.

       Alkyl polythiophene (P3UBT) THF solutions were used in the experiment as it yielded the most stable system. The pump powers used were between 0.5 - 10 μJ/pulse. Pump power was attenuated so as to avoid solvent signal (< 10 μJ/pulse).

References

[A3] J.Z Zhang, R.H O'Neil, T.W. Roberti, "Femtosecond studies of photoinduced electron dynamics at the liquid-solid interface of aqueous CdS colloids**.** Journal of Physical Chemistry, vol.98, (no.14), 7 April 1994, 3859-64.

Appendix IV

Renewable Energy and Photovoltaics Background

This project falls under the program area of Renewable Energy. It is thus useful to give some background on renewable energy and photovoltaic terminology. This can allow an overview of the technical and marketing challenges that this research is directed towards.

Fossil fuels like coal, natural gas and oil power our society, adding to the input of solar energy we receive daily. This "fossil" fuel reserve is finite. It is estimated that only a few hundred years supply are present at our current rate of burning, and the rate of consumption is increasing as developing nations compete for their share of the global economy. This resource problem aside, the use of these stored products of ancient photosynthesis is not without a price. As the carbon dioxide concentration in the atmosphere increases due to this fossil fuel consumption and deforestation, we are inadvertently returning the Earth to a state of high carbon dioxide concentration found when the sun was much weaker. It is predicted by the United Nations Intergovernmental Panel on Climate Change that the warming of the earth over the next 50 years could have devastating effects on sea levels, agriculture, climate, immigration and economic development. The benefits of diversifying our energy portfolio include those mentioned above, and economic benefits to both the United States and to California due to use of energy resources available locally (e.g. within California).

One method to achieve these benefits and to wean ourselves from fossil fuels is to re-create photosynthesis, and utilize the solar-energized electrons directly to produce fuels and electricity. Today, natural photosynthesis on the land and in the oceans produces eight times the current combined energy requirements of humanity. Converting solar energy at only 10 % efficiency using 1% of the Earth's land area would supply us with twice our current energy needs worldwide [A4, A5]. Over the past several decades, researchers have learned much about photosynthesis and about materials, and have begun to create solar converters of rivaling those of nature. Using current solar technologies, a square 161 kilometers (km) on a side located in the deserts near California could, during one year, produce the energy equivalent to that used annually in the entire United States. The challenge becomes the harvesting of this energy in an economically efficient way.

One renewable energy technology utilizes Photovoltaic (or PV) solar cells. PV solar cells convert incoming solar radiation directly into electricity. PV modules are large-area solid-state semiconductor devices that convert solar energy directly into electricity. The first photovoltaic cells were measured by Becquerel in 1839 and used copper oxide or silver halide coated metal electrodes immersed in an electrolyte solution. Modern solar cells were first developed in the 1950's and are widely used today to power satellites, villages as well as on buildings and in utility – scale power generation. These solar cells use a solid state junction which separates regions of electron (n) and hole (p)

conduction. Electrons and holes created via the absorption of light in a semiconductor diffuse at different rates within the cell and are eventually collected at the p-n junction. Individual PV modules produce direct-current (dc) electricity, and are available in 10-300 Watt sizes. Their actual power output depends upon the intensity of sunlight, the operating temperature of the module, and other factors. Additional components such as electrical switches, diode protection circuits, inverters, and batteries connect the PV output with the electrical load. The resulting assembly of components is known as the PV system. There are numerous advantages of solar cells, including their reliability, silence, long lifetime, low maintenance, flexibility and low pollution. Solar cells can also be incorporated as building materials in roofs and walls. Solar energy allows consumers to produce their own electricity and become more self-sufficient. Energy supply is then more distributed and would be less susceptible to breakdown or distribution. In general, solar energy can also help people have more control over their energy supply and be less dependent on centralized sources of power. PV systems could provide 'mini-utilities' to millions. Although PV systems involve high-tech manufacturing, the assembly, installation, and maintenance of PV systems does not require high skills or training. PV systems could provide local employment, in areas where it is most needed. This could play a part in helping achieve economic sustainability in a community.

One of the major problems with PV systems is that they are more expensive than traditional sources of electricity. Government subsidies and incentives can help reduce costs, but it will take time until the effects of economies of scale set in and production costs decrease. The cost of solar photovoltaics has dropped in price from over 100 dollars per peak watt in the 1970s to under $6/peak watt today. Types of solar panels have diversified, and now include 100 – 200 Watt modules of crystalline Silicon, amorphous Silicon, Cadmium Telluride, Copper Indium Diselenide, and others. The light energy to electrical energy conversion efficiency of PV panels typically ranges from 10 % to 15 %, with steadily increasing values over the last 20 years. With continued interest and investment the trend in increasing efficiencies, and decreasing costs is expected to continue. Growth in energy markets in the developing world has prompted energy giants such as British Petroleum, Kyocera, Siemens, and Shell to purchase PV manufacturers. Today, approximately 100 Megawatts of solar panels are produced and shipped. Still, this puts the per unit of energy at approximately 30 cents per kW-hr, about three to five times the cost of conventional sources in most locations.   A new thin film PV technology called the dye-sensitized nanocrystalline solar cell is based on organic dyes and is modeled after photosynthesis.

Dye Sensitized Nanocrystalline Solar Cell

A new kind of thin film PV solar cell, called a nanocrystalline dye sensitized solar cell [A6], is remarkable in that it resembles natural photosynthesis in two respects: 1) it uses an organic dye to absorb light and produce a flow of electrons, and 2) it uses multiple layers to enhance both the absorption and collection efficiencies of previous approaches. It is one of a new class of devices which are called molecular electronic devices otherwise known as nanotechnology. In the late 19th century, it was discovered

that certain organic dyes could extend the response of silver halide based photographic film to visible wavelengths. The mechanism has been found to involve the electron or energy transfer from the organic molecule to the semiconducting silver halide grain. This sensitization is the basis for modern photography. The nanocrystalline dye sensitized cell uses this type of sensitization to create an efficient, but not yet commercial, solar cell.

To create this newer generation solar cell, a solution of nanometer size particles of titanium dioxide, or TiO_2, is deposited directly on conductive glass by a process similar to that used in painting. In fact, one of the cheapest known large bandgap semiconductors, this abundant TiO_2 powder is currently used in white paints. The film is heated to form a porous, high surface area TiO_2 structure which resembles a thin sponge or membrane. This is used as a support as the glass plate is dipped into a solution of a dye such as a red ruthenium containing dye, or, alternatively, an anthocyanin, or green chlorophyll derivative. A single layer of dye molecules attaches to each particle of the TiO_2 and acts as the primary absorber of sunlight. To form the final cell, a drop of liquid electrolyte containing iodide is placed on the film to percolate into the pores of the membrane. A counter electrode of conductive glass, which has been coated with a thin catalytic layer of platinum or carbon, is placed on top, and the sandwich is illuminated through the TiO_2 side.

Organic dyes have previously been used for solar cells. Since the mobility of charge that are transported within the organic layer is so low, it was found that only a very thin layer was active for charge injection. This meant that if thicker layers were used to absorb more light, they would not proportionally add to the electrical output of the cell. What is new about the nanocrystalline cell is the use of a rough TiO_2 substrate for a thin layer of dye in order to increase the light absorption while allowing for efficient charge collection. Since the dye layer is so thin, the excited electrons produced from light absorption can be injected into the TiO_2 with near unity efficiency via sensitization. The TiO_2 therefore functions in a similar way as does the silver halide in photography except that, instead of forming an image, the injected electrons produce electricity. Because of the minute thickness of the dye, each layer of dye may not absorb very much light, but, like the leaves of a tree or the stacked thylakoid membrane found in photosynthesis, when added together, the many interconnected particles of the porous membrane can absorb 90% of visible light. The electrons lost by the dye are quickly replaced by the iodide in the electrolyte solution to produce iodine or triiodide, which in turn obtains an electron at the counter electrode after it has flowed through the load. The TiO_2 serves as the electron acceptor, and the iodide serves as the electron donor, with the dye functioning as a photochemical "pump." This configuration resembles the electron transfer found in natural photosynthesis.

PV Device Characteristics

A photovoltaic device can be modeled as an ideal diode in parallel with a light-induced current generator J_{SC}. This short circuit current is a function of the generation of

electron-hole pairs generated by the absorption of light and a function of the efficiency of their collection. The current as a function of voltage, V, and the J-V characteristics of a solar cell are given by

$$J(V) = \text{Diode Equation} - J_{SC} \qquad \text{A1}$$

This equation is also further modified to include resistive losses due to series and shunt resistances. Series resistance is due to the conductivity of the materials and the thickness of the various layers. Shunt resistances are due to the short circuit pathways that allow charge carries to recombine before they can be collected at the contacts and forced to due work in an external circuit. A current-voltage curve of a solar cell yields important operational parameters that are dependant on the above terms, among which are the short-circuit current J_{SC}, the open-circuit voltage V_{OC}, and the current and voltage at the maximum power point, J_{mp} and V_{mp}, respectively. The maximum power output of the solar cell is the product of J_{mp} and V_{mp}. The term called the fill factor, or FF, combines these terms, and is defined as

$$FF = \frac{V_{mp}J_{mp}}{V_{OC}J_{SC}} \qquad \text{A2}$$

For practical photovoltaic cells, the fill factor ranges from approximately 0.70 to 0.85. For a typical single-crystal silicon solar cell, we find, approximately, that V_{OC} = 0.588 V, J_{SC} = 35 mA/cm^2 and FF = 0.8. Thus a 100 cm^2 cell illuminated with 100 mW/cm^2 sunlight is capable of producing approximately 1.6 watts (e.g. 16% efficiency). Most practical applications would require more power. Fortunately, one can increase the voltage by adding more cells in series, and one can increase the current by wiring more cells in parallel. The challenge is to find ways of obtaining this power economically. The dye sensitized solar cell is one promising ways that this may be accomplished.

References

[A4] D. Pimentel, G. Rodriguez. "Renewable Energy: Economic and Environmental Issues," Bio. Sci., Vol. 44, No. 8. 536.
[A5] J. Turner, "A Realizable Renewable Energy Future", Science, 285, 30 July 1999 687.
[A6] M. K Nazerruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Mueller, P. Liska, N. Vlachopoulos, M. Grätzel, "Conversion of Light to Electricity by cis- SCN$_2$Bis(2, 2'bipyridyl-4,4'-dicarboxylate)ruthenium(II) Charge-Transfer Sensitizes (X=Cl-, Br-, I-, CN-, SCN-) on Nanocrystalline TiO2 Electrodes", J. Am. Chem. Soc. 1993, 115, 6382-6390.

Appendix V Estimated dye sensitized cell cost

As an estimate of the cost of this new cell, one considers the materials and fabrication costs associated with it's production. This is outlined in Table AV1, below, and uses costs for amorphous silicon thin film solar cells as a guide [A7]. The cost of the cell is estimated to lie in the range from $48 to $64 1993 dollars per square meter. The direct costs such as tools and labor are related to the actual production of the module, while the indirect costs such as accountants, rent, and computers are volume insensitive.

Table AV1— *G. Smestad et al. / Solar Energy Materials and Solar Cells 32 (1994) 259–272*

Nanocrystalline solar cell module cost estimate breakdown. The cost is calculated per unit module area

Item	Need per m^2	$ per m^2
TiO_2	10 g Anatase	0.03
Ru Dye	100 mg adsorbed	7–10
SnO_2:F Glass	2 m^2 (10 Ω/square)	30
Pt for counter electrode	3 monolayers	0.01
Electrolyte and iodide	50 ml	0.1–1
Additional costs:		
Production Overhead		
(Equipment Depreciation, Indirect and Other Direct Materials)		5–7
Labor (Direct and Indirect which includes assembly and testing)		0.3–0.5
Encapsulant or Sealant		2–3
Frame and electrical interconnects		2
Additional protective glass cover and Tedlar backing		2–3
Profit, Interest due on loans		0–8
Total module cost		48–64 $/$m^2$
Cost per peak Watt		0.48–0.80 $/Wp

This calculation assumes a 5-10 MW/year factory with 100 employees, and a capital cost of equipment of $17,000,000, housed in a 2,000 m2 facility. The module costs are determined primarily by the cost of the conductive glass, and the production overhead. To estimate the cost per peak watt, one relates the cost per unit area with the power produced, which depends on the solar conversion efficiency and the peak solar illumination. For the module alone, an 8 % efficient cell would produce power at 0.60 - 0.80 $/Peak Watt (Wp) if the module cost is 48 - 64 $/$m^2$. For a 10% efficient cell, the cost would be approximately 0.48 - 0.64 $/Wp. The estimate in 2001 dollars is modified to approximately $2/watt. As a comparison, the module costs for single crystal Silicon solar cells are now 3 - 8 $/Wp.

To produce useful power in a commercial application, one must consider the average illumination, instead of the peak, as well as the additional costs of land, batteries, support structures and the lifetime of the panel. If these Balance of Systems (BOS) costs are considered, the cost of power produced with this solar cell would be 0.07 - 0.10 $/kWh, assuming a 10 % efficient module which lasts at least 15 years under the illumination found in the western United States. These costs do not consider that the

nanocrystalline dye solar cell may be more easily recycled than conventional solar cells. Note that this cost lies in the range of electricity costs for conventional fossil fuel based systems, and thus the above analysis demonstrates that the nanocrystalline dye solar cell, if proven to be stable over 15 years, could represent a viable renewable energy option.

References

[A7] G. Smestad, "Testing of dye sensitized TiO_2 solar cells I & II", Solar Energy Materials and Solar Cells, **32**, 259, 1994.